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## DIELECTRIC CONSTANT OF LIQUID PARAHYDROGEN

BY R. J. CORRUCINI



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## ABSTRACT

It is shown that the available data on the dielectric constant of hydrogen conform to the Clausius-Mossotti equation within the probable experimental errors. The published data cover temperatures from the triple point ( $\sim 14^\circ\text{K}$ ) to well above room temperature and a thousandfold range of densities. Using an average value of the specific polarization, tables of the dielectric constant of the liquid have been computed for temperatures from the triple point ( $13.803^\circ\text{K}$ ) to  $32^\circ\text{K}$  ( $58^\circ\text{R}$ ) and pressures from saturation to 340 atmospheres.

# DIELECTRIC CONSTANT OF LIQUID PARAHYDROGEN

R. J. Corruccini

Introduction Capacitance measurements are used in liquid hydrogen technology to determine liquid level and apparent density. As will be shown, the dielectric constant is represented very well as a function of density by the well known Clausius-Mossotti equation. With the recent publication of extensive experimental data on the density and specific volume of parahydrogen<sup>1</sup> it has now become possible to compute the dielectric constant for a wide range of conditions. This note presents tables of dielectric constant as a function of pressure up to 340 atm (5000 psia) and as a function of temperature from the triple point to near the critical point. The basis of these calculations will now be presented.

The Clausius-Mossotti equation can be written

$$\frac{\epsilon - 1}{\epsilon + 2} v = p$$

in which

- $\epsilon$  is the dielectric constant
- $v$  is the specific volume
- $p$  is the specific polarization, a property of the substance having the same dimensions as  $v$ .

To the extent that  $p$  is a constant for a given substance, the substance may be said to obey the Clausius-Mossotti equation. The equation is derived from classical electrostatic theory on the assumptions that the molecules are non-polar and spherical, there are no short-range interactions between them, and their spatial distribution is isotropic<sup>2, 3</sup>. Hydrogen satisfies only the first assumption. However, errors due to the other assumptions tend to vanish as the density increases<sup>4</sup> and are negligible for non-polar gases at ordinary pressures. More complete theories have been developed<sup>4, 17, 18</sup> that are valid up to moderate densities, but none that are generally accurate at densities characteristic of liquids.

Thus, in applying the equation to liquid hydrogen, deviations certainly are to be expected due to violation of all of the assumptions previously stated except the first. However, it is found that all of the available data can be represented within the probable experimental

errors by a single value of the polarization, even though they cover a thousandfold range of densities. Now the available experimental data will be examined.

Liquid hydrogen. Of five known references, three are from Leiden. A reading of the most recent of the three (Werner and Keesom, 1925<sup>5</sup>) and examination of the scatter of the various  $\epsilon$  and  $p$  values shows clearly that the earlier two (by Breit and Onnes, 1924 and Wolfke and Onnes, 1924) now should be given no weight. Measurements by Guillien<sup>6</sup> appear to be comparable in precision and accuracy to those of Werner and Keesom. Both of these papers cover the range, 14-20.4°K, and the authors conclude that their data show no consistent variations in  $p$  that could be interpreted as deviations from the Clausius-Mossotti equation. To these should be added a value at the boiling point by van Itterbeek and Spaepen<sup>7</sup> of apparently comparable reliability. Mean values of  $p$  obtained in these investigations are given in table 1.

In addition it is possible to compute the dielectric constant from refractive index data using the relation,  $\epsilon = n_{\infty}^2$ , where  $n_{\infty}$  is the refractive index extrapolated to very long wavelengths. Johns and Wilhelm<sup>8</sup> have measured the refractive index of liquid hydrogen from 14° to 20.4°K at wavelengths in the visible region. Guillien<sup>6</sup> has calculated the value,  $n_{\infty}^2 = 1.2288 \pm .0003$  at 20.4°, from their data. The corresponding value of  $p$  calculated using the specific volume of normal hydrogen<sup>9</sup> is shown in table 1.

Solid hydrogen. The data of Werner and Keesom<sup>5</sup> disagree markedly with those of Guillien.<sup>6</sup> From Guillien's work and similar experiences at this laboratory in measuring the dielectric constant of liquid and solid nitrogen,<sup>10</sup> it is clear that discrepancies of this kind readily occur due to the difficulty of ensuring that the solid, which has to be cast in place in the measuring condenser, is free from voids. In order to obtain a meaningful test of the Clausius-Mossotti equation using a solid, either extreme care must be taken with the preparation of the sample, or else its effective density must be determined in place by an independent method.

Gaseous hydrogen. There have been many direct measurements of the dielectric constant of the gas; most of them near ambient temperature and pressure. However, Maryott and Buckley<sup>11</sup> in providing a "best" value at 20°C and 1 atmosphere have

based it entirely on optical and microwave measurements of the refractive index using the relation,  $\epsilon = n_{\infty}^2$ . Maryott and Buckley dismiss the direct measurements of  $\epsilon$  with this statement: "In a majority of cases, values of the dielectric constant measured at radio frequencies do not appear to be of sufficient accuracy to provide useful information for reference purposes." A value of  $p$  calculated from Maryott and Buckley's recommended dielectric constant using the specific volume of the real gas<sup>9</sup> is presented in table 1.

Of special interest to this inquiry are those few studies of the dielectric constant that cover wide ranges of temperature, pressure and density. The extremes of temperature are represented by the work of van Itterbeek and Spaepen<sup>12</sup> (20° - 291°K) and Forro<sup>13</sup> (295° - 571°K). Each of these authors obtained constant values of  $p$  within their experimental limits of accuracy. A more rigorous test is provided by the data of Michels, Sanders and Schipper<sup>14</sup> at 25° and 100°C and at pressures from 1 to 1425 atm. The maximum density achieved equals that of saturated liquid at 26°K. In spite of the great range of densities covered by Michels et al, the polarization showed no discernible trend with density or temperature. Their average value is included in table 1.

Summary of experimental results. The following table summarizes the experimental results that are regarded as especially significant. As indicated, some of the tolerances attached to the mean values of polarization are based on estimates of accuracy by the original authors. Others are guesses by the present author. In most cases, the stated tolerance is approximately equal to the mean deviation of several determinations. None of the investigators referred to the matter of ortho-para composition, and so it is assumed that the samples were normal hydrogen in all cases.

Inasmuch as none of the researches showed internal evidence of dependence of  $p$  upon the experimental conditions, the variations in  $p$  among the various investigations shown in table 1 cannot be construed as evidence for deviations from the Clausius-Mossotti equation. Parts of the discrepancies may be attributed to the use of different data for the specific volumes and to accidental variations in ortho-para composition. However, the discrepancies are too large to be fully accounted for in these ways, and in large part must be charged to undisclosed systematic errors in the experiments.

Table 1  
Specific Polarization of Hydrogen

Reference	State	Temperature °K	Approx. Range of Specific Volume $\text{cm}^3/\text{g.}$	p $\text{cm}^3/\text{g.}$
Werner & Keesom <sup>5</sup> 1925	Liq.	14 - 20.4	13-14	1.010 $\pm$ .002**
Guillien <sup>6</sup> 1940	Liq.	14 - 20.4	13-14	0.9984 $\pm$ .002**
Van Itterbeek & Spaepen <sup>7</sup> 1942	Liq.	20.4	14	0.988 $\pm$ .003**
Johns & Wilhelm <sup>8,6</sup> 1937	Liq.	20.4	14	*0.9986 $\pm$ .001**
Maryott & Buckley <sup>11</sup> 1953	Gas	$\sim$ 293	12,000	*1.0104 $\pm$ .001
Michels, et al <sup>14</sup> 1953	Gas	298, 373	16-11,000	1.001 $\pm$ .002

\*From measurements of refractive index.

\*\*Based on estimate of accuracy by original authors

The degree of constancy of polarization that has been demonstrated for hydrogen is rather exceptional and raises the question of how well the Clausius-Mossotti equation might fit other cryogenic fluids. Böttcher<sup>2</sup>(p.209) attributes this result to hydrogen having an exceptionally small value of the imperfection parameter,  $\alpha/a^3$ , where  $a$  is the average molecular radius, and the "polarizability",  $\alpha$ , is given by  $P = Mp = 4/3 \pi N\alpha$ , in which  $N$  is Avogadro's number, and  $M$  is the molecular weight. Conversely, the imperfection parameter is larger for carbon dioxide, and, accordingly, the polarization of this gas has been found to vary with pressure by about 2% in 150 atm. Values of these quantities for some cryogenic substances are shown in table 2. The trend of  $\alpha/a^3$  suggests that nitrogen and oxygen will show relative deviations from the Clausius-Mossotti equation intermediate between those of hydrogen and carbon dioxide, while helium should show even less deviation than hydrogen.

Table 2  
Imperfection Parameters

Substance	P	$10^{24}\alpha$	* $\alpha$	$\alpha/a^3$
	$\text{cm}^3/\text{mol}$	$\text{cm}^3$	$\text{\AA}$	
He	0.51	0.20	1.28	0.10
H <sub>2</sub>	2.02	0.79	1.47	0.25
N <sub>2</sub>	4.3	1.71	1.85	0.27
O <sub>2</sub>	4.0	1.59	1.76	0.29
CO <sub>2</sub>	7.3	2.89	2.1	0.31

\* Based on a collection<sup>15</sup> of values determined from second virial coefficients and viscosities. Those determined from second virial coefficients were given greater weight.

Tables of dielectric constant. A value of  $p$  of  $1.00 \text{ cm}^3/\text{g}$  ( $0.0160 \text{ ft}^3/\text{lb}$ ) is seen to represent the experimental results listed in table 1 within about  $\pm 1\%$ . This value has been used to calculate tables 3-7 using the Clausius-Mossotti formula,

$$\epsilon = \frac{v + 2p}{v - p}$$



and recently published provisional values<sup>1</sup> of the specific volume of parahydrogen. The latter are estimated to be accurate within 0.2%<sup>16</sup> except near the critical point, where the equation of state used to represent the data introduced systematic errors. The deviations due to the equation of state were eliminated from the few values of specific volume near the critical point before calculating the dielectric constant. Consequently, the error in  $\epsilon$  is almost entirely due to the one percent uncertainty in  $p$ . The error in  $(\epsilon - 1)$  from this source is also about one percent, while the error in  $\epsilon$  is estimated to range from 0.15% at the lowest density to 0.25% at the highest. It should be noted that the densities at the higher pressures (below the stepped lines in tables 3 and 6) exceed the maximum density at which the dielectric constant has been experimentally measured by as much as 15%. The validity of the adopted value of  $p$  at these higher densities has not been established.

Table 3 Dielectric Constant of Liquid Parahydrogen vs. Temperature (°K) and Pressure (atm)

P atm	T, °K	20	21	22	23	24	25	26	27	28	29	30	31	32
1		1.2297												
2		1.2302	1.2260	1.2216										
3		1.2306	1.2265	1.2221	1.2174	1.2122								
4		1.2311	1.2270	1.2227	1.2180	1.2129	1.2073	1.2010						
5		1.2315	1.2275	1.2233	1.2186	1.2136	1.2081	1.2020	1.1950					
6		1.2320	1.2280	1.2238	1.2192	1.2143	1.2089	1.2029	1.1962	1.1883				
7		1.2324	1.2285	1.2243	1.2198	1.2150	1.2097	1.2039	1.1973	1.1897	1.1805			
8		1.2329	1.2290	1.2249	1.2204	1.2157	1.2105	1.2048	1.1984	1.1911	1.1824			
9		1.2333	1.2295	1.2254	1.2210	1.2163	1.2112	1.2056	1.1994	1.1924	1.1842	1.1734		
10		1.2337	1.2300	1.2259	1.2216	1.2169	1.2119	1.2065	1.2004	1.1936	1.1857	1.1758	1.1621	
15		1.2358	1.2322	1.2284	1.2243	1.2200	1.2153	1.2103	1.2049	1.1990	1.1924	1.1847	1.1758	1.1645
20		1.2378	1.2343	1.2307	1.2268	1.2227	1.2184	1.2137	1.2088	1.2034	1.1976	1.1913	1.1839	1.1757
25		1.2396	1.2363	1.2328	1.2291	1.2253	1.2211	1.2168	1.2122	1.2073	1.2021	1.1964	1.1903	1.1832
30		1.2414	1.2382	1.2349	1.2313	1.2276	1.2237	1.2196	1.2153	1.2107	1.2059	1.2008	1.1952	1.1891
35		1.2431	1.2400	1.2368	1.2334	1.2298	1.2261	1.2222	1.2181	1.2138	1.2093	1.2046	1.1995	1.1942
40		1.2448	1.2418	1.2386	1.2354	1.2319	1.2284	1.2246	1.2208	1.2167	1.2124	1.2080	1.2033	1.1984
45		1.2464	1.2434	1.2404	1.2372	1.2339	1.2305	1.2269	1.2232	1.2193	1.2153	1.2111	1.2067	1.2021
50		1.2479	1.2450	1.2421	1.2390	1.2358	1.2325	1.2291	1.2255	1.2218	1.2179	1.2139	1.2098	1.2055
60		1.2508	1.2481	1.2453	1.2424	1.2394	1.2363	1.2331	1.2297	1.2263	1.2227	1.2191	1.2153	1.2114
70		1.2535	1.2510	1.2483	1.2455	1.2427	1.2397	1.2367	1.2336	1.2303	1.2270	1.2236	1.2201	1.2165
80		1.2561	1.2536	1.2511	1.2484	1.2457	1.2429	1.2400	1.2371	1.2340	1.2309	1.2277	1.2244	1.2211
90		1.2585	1.2561	1.2537	1.2512	1.2486	1.2459	1.2431	1.2403	1.2374	1.2345	1.2315	1.2284	1.2252
100		1.2608	1.2586	1.2562	1.2538	1.2513	1.2487	1.2461	1.2434	1.2406	1.2378	1.2349	1.2320	1.2290
120		1.2652	1.2631	1.2609	1.2586	1.2563	1.2539	1.2514	1.2489	1.2464	1.2438	1.2412	1.2385	1.2357
140		1.2693	1.2672	1.2651	1.2630	1.2608	1.2586	1.2563	1.2540	1.2516	1.2492	1.2467	1.2442	1.2417
160		1.2730	1.2711	1.2691	1.2671	1.2650	1.2629	1.2607	1.2585	1.2563	1.2540	1.2517	1.2494	1.2470
180		1.2766	1.2747	1.2728	1.2709	1.2689	1.2669	1.2649	1.2628	1.2606	1.2585	1.2563	1.2541	1.2518
200		1.2799	1.2781	1.2763	1.2745	1.2726	1.2707	1.2687	1.2667	1.2647	1.2626	1.2605	1.2584	1.2563
220		1.2831	1.2814	1.2796	1.2779	1.2760	1.2742	1.2723	1.2704	1.2685	1.2665	1.2645	1.2625	1.2605
240		1.2845	1.2828	1.2811	1.2793	1.2775	1.2757	1.2739	1.2720	1.2701	1.2682	1.2663	1.2643	1.2623
260		1.2874	1.2858	1.2841	1.2824	1.2807	1.2790	1.2772	1.2754	1.2736	1.2717	1.2699	1.2680	1.2660
280			1.2886	1.2870	1.2853	1.2837	1.2821	1.2803	1.2786	1.2768	1.2751	1.2733	1.2714	1.2695
300			1.2914	1.2898	1.2882	1.2866	1.2850	1.2833	1.2817	1.2800	1.2782	1.2765	1.2747	1.2729
320				1.2925	1.2910	1.2894	1.2878	1.2862	1.2846	1.2829	1.2813	1.2796	1.2779	1.2761
340				1.2951	1.2936	1.2921	1.2905	1.2890	1.2874	1.2858	1.2842	1.2825	1.2809	1.2791

Note: Values below the dotted line are estimated.

Table 4. Dielectric Constant of Saturated Liquid  
Parahydrogen vs. Temperature (°K)

T, °K	ε	T, °K	ε
13.803 *	1.2503	23	1.2168
14	1.2497	24	1.2119
15	1.2467	25	1.2067
16	1.2436	26	1.2011
17	1.2403	27	1.1949
18	1.2369	28	1.1880
19	1.2333	29	1.1802
20	1.2295	30	1.1710
20.268**	1.2285	31	1.1598
21	1.2255	32	1.1444
22	1.2213		

\* Triple point

\*\* Normal boiling point

Table 5. Dielectric Constant of Saturated Liquid  
Parahydrogen vs. Pressure (atm)

P, atm.	ε	P, atm.	ε
1	1.2285	6	1.1865
2	1.2175	7	1.1794
3	1.2087	8	1.1720
4	1.2010	9	1.1641
5	1.1937	10	1.1553

Table 6 Dielectric Constant of Liquid Parahydrogen vs. Temperature (°R) and Pressure (psia)

P psia	T, °R	36	38	40	42	44	46	48	50	52	54	56	58
15		1.2294											
20		1.2296	1.2249										
30		1.2299	1.2253	1.2203									
40		1.2302	1.2257	1.2207	1.2152								
50		1.2305	1.2260	1.2211	1.2157	1.2097							
60		1.2308	1.2263	1.2215	1.2161	1.2102	1.2036						
70		1.2311	1.2267	1.2218	1.2166	1.2108	1.2043	1.1969					
80		1.2314	1.2271	1.2222	1.2170	1.2113	1.2050	1.1977					
90		1.2318	1.2274	1.2226	1.2175	1.2118	1.2056	1.1984	1.1901				
100		1.2321	1.2277	1.2229	1.2179	1.2123	1.2062	1.1992	1.1910	1.1811			
120		1.2327	1.2284	1.2237	1.2187	1.2132	1.2073	1.2005	1.1928	1.1836	1.1710		
140		1.2332	1.2290	1.2244	1.2195	1.2142	1.2083	1.2018	1.1945	1.1858	1.1745		
160		1.2338	1.2297	1.2251	1.2203	1.2151	1.2093	1.2030	1.1960	1.1877	1.1774	1.1635	
180		1.2344	1.2303	1.2259	1.2211	1.2159	1.2103	1.2043	1.1974	1.1896	1.1800	1.1678	
200		1.2349	1.2309	1.2265	1.2218	1.2168	1.2114	1.2055	1.1988	1.1913	1.1824	1.1714	
250		1.2363	1.2323	1.2281	1.2237	1.2189	1.2137	1.2081	1.2019	1.1951	1.1873	1.1782	1.1671
300		1.2376	1.2338	1.2297	1.2254	1.2208	1.2158	1.2105	1.2048	1.1984	1.1915	1.1835	1.1742
350		1.2389	1.2352	1.2312	1.2271	1.2226	1.2178	1.2128	1.2073	1.2014	1.1951	1.1879	1.1797
400		1.2401	1.2365	1.2327	1.2286	1.2243	1.2197	1.2149	1.2097	1.2042	1.1982	1.1917	1.1843
450		1.2413	1.2377	1.2340	1.2301	1.2259	1.2215	1.2169	1.2119	1.2067	1.2010	1.1950	1.1882
500		1.2425	1.2390	1.2354	1.2315	1.2275	1.2233	1.2188	1.2140	1.2090	1.2036	1.1979	1.1918
600		1.2448	1.2414	1.2380	1.2343	1.2304	1.2264	1.2222	1.2178	1.2131	1.2082	1.2031	1.1977
700		1.2469	1.2437	1.2404	1.2368	1.2331	1.2293	1.2254	1.2212	1.2169	1.2124	1.2076	1.2026
800		1.2489	1.2458	1.2426	1.2392	1.2358	1.2321	1.2284	1.2244	1.2203	1.2160	1.2116	1.2070
900		1.2508	1.2478	1.2448	1.2415	1.2382	1.2346	1.2311	1.2273	1.2235	1.2194	1.2152	1.2109
1000		1.2526	1.2497	1.2468	1.2437	1.2405	1.2370	1.2336	1.2300	1.2263	1.2225	1.2186	1.2145
1250		1.2570	1.2544	1.2516	1.2487	1.2456	1.2425	1.2394	1.2361	1.2328	1.2293	1.2259	1.2222
1500		1.2610	1.2585	1.2559	1.2532	1.2504	1.2476	1.2446	1.2416	1.2385	1.2353	1.2321	1.2288
1750		1.2648	1.2623	1.2599	1.2573	1.2546	1.2520	1.2492	1.2464	1.2435	1.2406	1.2376	1.2345
2000		1.2682	1.2659	1.2636	1.2612	1.2586	1.2561	1.2534	1.2508	1.2481	1.2454	1.2425	1.2396
2500		1.2744	1.2724	1.2703	1.2680	1.2658	1.2635	1.2612	1.2588	1.2563	1.2537	1.2512	1.2487
3000		1.2802	1.2783	1.2763	1.2743	1.2721	1.2700	1.2679	1.2656	1.2633	1.2610	1.2588	1.2564
3500		1.2837	1.2817	1.2799	1.2779	1.2759	1.2738	1.2718	1.2697	1.2676	1.2653	1.2632	
4000			1.2867	1.2851	1.2832	1.2812	1.2793	1.2775	1.2754	1.2735	1.2713	1.2693	
4500				1.2899	1.2881	1.2862	1.2844	1.2826	1.2807	1.2789	1.2769	1.2749	
5000					1.2943	1.2925	1.2909	1.2892	1.2874	1.2855	1.2839	1.2820	

Note: Values below the stepped line represent an extrapolation of p with density.

Table 7.

Dielectric Constant of  
Saturated Liquid Parahydrogen  
vs. Pressure (psia)

P psia	T °R	ε
10	34.260	1.2329
15	36.603	1.2279
20	38.436	1.2238
30	41.291	1.2168
40	43.529	1.2108
50	45.400	1.2053
60	47.022	1.2001
70	48.464	1.1951
80	49.768	1.1902
90	50.962	1.1854
100	52.067	1.1806
120	54.062	1.1705
140	55.832	1.1594
160	57.424	1.1461
180	58.860	1.1257

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